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Group III Materials: New Phases and Nano-particles with Applications in Electronics and Optoelectronics

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Final Report

Long-term Research Goal

Development of a molecular understanding of (a) the control exerted by a molecular precursor over the structure of a solid state material and (b) the complexation and surface modification of semiconductor surfaces.

S&T Objectives

1. Demonstrate molecular control for the MOCVD growth of gallium and indium chalcogenides.
2. Demonstrate a molecular model approach to the prediction of suitable binding groups to semiconductor surfaces.
3. Demonstrate the application of surface coordination chemistry to the control over the electronic properties of semiconductor nano-particles.

Approach

We have chosen to perform our research using a combination of traditional organometallic chemistry and materials science. We are attempting to exploit the chemical control allowed by synthetic chemistry towards the control of electronic properties. For example, we have investigated the MOCVD growth of gallium and indium chalcogenides using pre-chosen molecular templates.

S&T Completed

Volatility trends are established for a series of organometallic molecular solids with a cubane geometry and the general form $[(R)Ga(\mu_3-E)]_4$, where $R = Me_3C$ (tBu), $EtMe_2C$, Et_2MeC , or Et_3C and $E = S, Se, \text{ or } Te$. While the temperature of volatilization, T_{20} defined as 20 % mass loss from thermogravimetric analysis, was found to generally increase in a linear fashion with respect to increasing molecular mass, perturbations were observed that can be attributed to intermolecular ligand interactions. Sublimation enthalpies (ΔH_{sub}) for each cubane were calculated from thermogravimetric data, which show that the dependence of ΔH_{sub} on the degree of branching of the alkyl ligand appears to be more substantial than molecular mass effects alone. The C-H...H-C van der Waals interactions between alkyl substituents are estimated to account for more than 60 % of the ΔH_{sub} in the organometallic cubane system, $[(R)Ga(\mu_3-E)]_4$. Calculations based on the number of hydrogen atoms present in each alkyl yields an approximate value of *ca.* 4 kJ.mol⁻¹ for each C-H...H-C interactions. Using the TGA sublimation data vapor pressures may be calculated for each of the cubane compounds over a wide range of temperatures. All new cubanes have been characterized by MS, NMR, IR, and TG/DTA. The molecular structures of $[(Et_3C)_2Ga(\mu-Cl)]_2$, $[(Et_3C)Ga(\mu_3-S)]_4$, and $[(Et_3C)Ga(\mu_3-Se)]_4$ have been determined by X-ray crystallography.

The gallium-chalcogen-heterocubanes $[Cp^*Ga(\mu_3-E)]_4$, $E = S$ (1), Se (2), and $[Cp^+Ga(\mu_3-Se)]_4$ (3), have been synthesized by dehalosilylation reactions between $E(SiMe_3)_2$ ($E = S, Se$) and $RGaCl_2$, $R = Cp^*$ (C_5Me_5) and Cp^+ (C_5Me_4Et), and are characterized by elemental analyses, NMR spectroscopy, and mass spectrometry. The structure of compound 2 was determined by X-ray diffraction. The use of compounds 1 and 2 as single source MOCVD precursors for the low temperature growth of Ga_2E_3 films at 290 - 310 °C is described. The as-deposited films were amorphous, however, upon thermal annealing (500 °C) the films crystallized to the thermodynamic cubic phases. The corresponding tellurium analog decomposed in the solid state at 220 °C forming a gallium rich product.

Gallium selenide (GaSe) thin films have been grown at 325 - 370 °C by atmospheric pressure metal-organic chemical vapor deposition (AP-MOCVD) using the single source precursors $[(R)Ga(\mu_3-Se)]_4$ ($R = CMe_3$, $CtEtMe_2$, and $CtEt_2Me$). In contrast, the growth of gallium telluride from $[(R)Ga(\mu_3-Te)]_4$ is accomplished at 285 - 310 °C by low pressure metal-organic chemical vapor deposition (LP-MOCVD). Characterization of the films by Auger electron spectroscopy (AES), Rutherford backscattering (RBS), and wavelength dispersive

spectroscopy (WDS) microprobe analysis shows all the films to have Ga:E (E = Se, Te) compositions of 1:1 with a low degree of impurities (C < 2 %; O < 0.1 %). From X-ray diffraction (XRD) and transmission electron microscopy (TEM) the GaSe and GaTe films were found to be polycrystalline hexagonal layered GaE structures, with a preferred *c*-axis orientation independent of substrate. For GaSe this represents the thermodynamically stable phase, while hexagonal-GaTe is a metastable phase that converts to the thermodynamic monoclinic form on annealing at 500 °C. Diffraction results yield appropriate lattice parameters of *a* = 4.1 Å (TEM) and *c* = 16.38 Å (XRD) for hexagonal GaTe. Crystallite and particle size measurements reveal that the as-deposited films consist of oriented *ca.* 10 nm crystalline particles. The formation of these hexagonal layered structures is proposed to occur as a consequence of the fragmentation of the cubane's Ga₄E₄ core during deposition, and the formation of trimeric "Ga₃E₃" building blocks.

The reaction of Ga(^tBu)₃ with 1 molar equivalent of a carboxylic acid yields the carboxylate bridged dimeric compounds, [(^tBu)₂Ga(μ-O₂CR)]₂, where R = Ph (3), C₆H₄-3-CN (4), and C₆H₄-3-Br (5), respectively. Similarly, reaction of Ga(^tBu)₃ with HSPH yields the thiolate bridged compound, [(^tBu)₂Ga(μ-SPh)]₂ (6). The molecular structures of compounds 3, 4, and 6 have been determined by X-ray crystallography. The Ga...Ga and Ga-ligand inter-atomic distances for these compounds, as well as group 15 and 16 donor bridging ligands, are compared to the values for the surface of GaAs and cubic-GaS in order to determine their suitability as linkage groups for self-assembled monolayers.

Gallium and indium selenide nanoparticles have been grown during metal organic chemical vapor deposition (MOCVD) of films from the single source precursors [(^tBu)GaSe]₄ and [(EtMe₂C)InSe]₄, respectively. Vapor phase decomposition of the precursors leads to thermodynamic phase formation as well as particle formation.

A range of In-Se bond forming reactions have been investigated, including: insertion of selenium into either an In-C or In-S bond, reaction of an indium halide with a magnesium selenolate, and via chlorosilane elimination. The reaction of In(^tBu)₃ with Se yields [(^tBu)₂In(μ-Se^tBu)]₂ (9) and [(^tBu)In(μ₃-Se)]₄ (10). In contrast, the reaction of In(CMe₂Et)₃ (7) and In(ⁿBu)₃ with Se preferentially forms [(Me₂EtC)In(μ₃-Se)]₄ (11) and [(ⁿBu)In(μ₃-Se)]₄ (12), respectively. The reaction of compound 7 with Te yields [(Me₂EtC)In(μ₃-Te)]₄ (13). Compound 10 is also formed from the reaction of [(^tBu)₂In(μ-S^tBu)]₂ with either Se or Se=PPh₃, while both compounds 9 and 10 may be prepared from the reaction of [(^tBu)₂In(μ-Cl)]_n with (^tBuSe)MgCl. Similarly, [(ⁿBu)₂In(μ-Se^tBu)]₂ (14) may be prepared from [(ⁿBu)₂In(μ-Cl)]₂. However, reaction of [(Me₂EtC)₂In(μ-Cl)]₂ with (^tBuE)MgCl (E = S, Se, Te) yields [(Me₂EtC)In(μ₃-S)]₄ (15) compound 11, and compound 13, respectively. Reaction of [(^tBu)₂M(μ-Cl)]_n (M = In, Ga) with Se(SiMe₃)₂ yields the silyl selenolate compounds, [(^tBu)₂M(μ-SeSiMe₃)]₂, M = In (16) and Ga (17). The various In-Se bond forming reactions are compared. The molecular structures of compound 9 and [(^tBu)₂In(μ-S^tBu)]₂ have been determined by X-ray crystallography.

The solid state structure of di-*tert*-butyl indium chloride, [(^tBu)₂In(μ-Cl)]_n, has been determined by X-ray diffraction, and consists of polymeric [-In-Cl-]_∞ chains arranged in an unusual saw-tooth pattern motif. The indium atom is in a severely distorted coordination environment approximated as a capped trigonal planar geometry. The structure of [(^tBu)₂In(μ-Cl)]_∞ is compared to [(Me)₂In(μ-Cl)]_∞.

Indium selenide (InSe) thin films have been grown at 230 - 420 °C by low pressure metal-organic chemical vapor deposition (MOCVD) using the single source precursors [(^tBu)₂In(μ-Se^tBu)]₂ and [(Me₂EtC)In(μ₃-Se)]₄. Characterization of the films by energy dispersive X-ray analysis (EDX) showed those grown from [(^tBu)₂In(μ-Se^tBu)]₂ to be indium rich, while those grown from [(Me₂EtC)In(μ₃-Se)]₄ are stoichiometric InSe. Transmission electron microscopy (TEM) indicates that the film morphology and crystallinity are highly dependent on the precursor and the deposition temperature. At low temperatures < 330 °C ball-like morphologies are observed, while deposition at 350 - 370 °C results in highly crystalline textured films. Use of [(^tBu)In(μ₃-Se)]₄ as the precursor at 320 - 420 °C results in indium metal films. The relationship between the precursor's structure and the film's morphology and chemical

composition are discussed. The efficacy of the single source precursor approach is considered with respect to elemental composition, phase formation, and film morphology.

The reaction of $\text{Ga}(\text{tBu})_3$ with phenylphosphonic acid results in the formation of the unusual phosphonate bridged dimer, $[(\text{tBu})_2\text{Ga}\{\mu\text{-O}_2\text{P}(\text{Ph})\text{OGa}(\text{tBu})_2\}]_2$, whose molecular structure consists two four-coordinate and two three-coordinate gallium centers. While $[(\text{tBu})_2\text{Ga}\{\mu\text{-O}_2\text{P}(\text{Ph})\text{OGa}(\text{tBu})_2\}]_2$ exists as the *trans* isomer in the solid state, it undergoes a *trans* to *cis* isomerization in solution, $\Delta H = 7 \pm 1 \text{ kJ.mol}^{-1}$ and $\Delta S = 25 \pm 4 \text{ J.mol}^{-1}.\text{K}^{-1}$.

The reaction of $[(\text{tBu})_2\text{Ga}(\mu\text{-Cl})]_2$ with 1 molar equivalent of $\text{Na}(\text{S}_2\text{CNR}_2)$ yields the di-*tert*-butyl gallium dithiocarbamate compounds $(\text{tBu})_2\text{Ga}(\text{S}_2\text{CNR}_2)_2$, $\text{R} = \text{Me}$ (18), Et (20), ^nPr (22). The *tert*-butyl gallium bis-dithiocarbamate compounds, $(\text{tBu})\text{Ga}(\text{S}_2\text{CNR}_2)_2$, $\text{R} = \text{Me}$ (19), Et (21), ^nPr (23), are formed as minor products. Separation of $(\text{tBu})_2\text{Ga}(\text{S}_2\text{CNR}_2)_2$ from $(\text{tBu})\text{Ga}(\text{S}_2\text{CNR}_2)_2$ may be readily accomplished by sublimation of the former. Compounds 18 and 20 are low melting point solids allowing their ready use as liquid precursors for MOCVD. The vaporization enthalpies (ΔH_v) have been determined, by thermogravimetric methods, for compounds 18, 20, 22, $(^n\text{Bu})_2\text{Ga}(\text{S}_2\text{CNMe}_2)_2$ (24) and $(^{\text{sec}}\text{Bu})_2\text{Ga}(\text{S}_2\text{CNMe}_2)_2$ (25), and are dependent on both the identity of the substituents on gallium and the dithiocarbamate ligand. An inverse relationship is observed between the ΔH_v and the extent of branching of the gallium alkyl. The molecular structures of compounds 18 and 20 have been determined by X-ray crystallography. Gallium sulfide (GaS) thin films have been grown at 375 - 425 °C by atmospheric pressure metal-organic chemical vapor deposition (AP-MOCVD) using compound 18. Characterization of the films by wavelength dispersive spectroscopy (WDS) microprobe analysis shows the films to have Ga:S compositions of 1:1 with a low degree of impurities ($\text{C} < 3\%$; $\text{O} < 1\%$). Gallium rich films were grown from compound 3 using AP-MOCVD and from compound 18 under reduced pressure. XPS studies of the GaS films additionally show an abundance of N on the surface, which has been confirmed to be present throughout the thin film by SIMS measurements. From X-ray diffraction (XRD) and transmission electron microscopy (TEM) the GaS films were found to be a new distorted hexagonal wurtzite phase ($a = 4.590 \text{ \AA}$, $c = 6.195 \text{ \AA}$).

The molecular structures of $(\text{tBu})\text{Ga}(\text{S}_2\text{CN}^n\text{Pr}_2)_2$ (19) and $(\text{iPrO})\text{Ga}(\text{S}_2\text{CNEt}_2)_2$ (26) have been determined. The variation in the geometries observed for bis-dithiocarbamate compounds of gallium, $(\text{X})\text{Ga}(\text{S}_2\text{CNMe}_2)_2$ ($\text{X} = \text{Cl}$, ^iPrO , tBu) do not lie along the Berry pseudo-rotation pathway for the square-based pyramid to trigonal bipyramid geometrical transition. Instead, the structures appear to lie on an unusual ligand two-step, "Texas", pseudorotation mechanism which results in a highly distorted trigonal bipyramidal geometry.

The *tert*-butyl substituted compounds of gallium have been synthesized and characterized: $[(\text{tBu})_2\text{Ga}\{\mu\text{-OCH}(\text{CF}_3)_2\}]_2$ (27), $[(\text{tBu})_2\text{Ga}(\mu\text{-O}_2\text{CET})]_2$ (28), $[(\text{tBu})_2\text{Ga}(\mu\text{-O}_2\text{CCF}_3)]_2$ (29), $[(\text{tBu})_2\text{Ga}\{\mu\text{-OC}(\text{Ph})\text{N}(\text{H})\}]_2$ (30), $[(\text{tBu})_2\text{Ga}\{\mu\text{-OC}(\text{Me})\text{NPh}\}]_2$ (31), $(\text{tBu})_3\text{Ga}[\text{OC}(\text{Ph})\text{NMe}_2]$ (32), $(\text{tBu})_3\text{Ga}[\text{OP}(\text{Ph})_2\text{NH}(^n\text{Pr})]$ (33), $(\text{tBu})_2\text{Ga}[\text{ON}(\text{H})\text{C}(\text{O})\text{Ph}]$ (34), $[(\text{tBu})_2\text{Ga}\{\mu\text{-O}_2\text{S}(\text{CF}_3)\text{O}\}]_2$ (35), $(\text{tBu})_2\text{Ga}(\mu\text{-Cl})_2\text{Li}(\text{HO}^i\text{Pr})_2$ (36), and $[\text{Li}(\text{HO}^i\text{Pr})_4][(\text{tBu})_2\text{GaCl}_2]$ (37). X-ray crystallographic characterization was obtained for compounds 27 - 32 and 34 - 37. Compounds 36 and 37 exhibit three dimensional hydrogen bonded networks in which augmentation of the $\text{O-H}\cdots\text{Cl}$ hydrogen bond is proposed to be due to the increased acidity of alcohols bonded to the Lewis acidic lithium ions. A discussion of the dependence of the puckering of the chair-like conformation in eight-membered cyclic compounds of the Group 13 metals is presented.

The vapor phase structures of $\text{Al}(\text{tBu})_3$ and $\text{Ga}(\text{tBu})_3$ have been investigated by gas phase electron diffraction and consist of planar three-coordinate monomers. Salient structural parameters (r_a) include: $\text{Al-C} = 2.005(3) \text{ \AA}$, $\text{Ga-C} = 2.034(2) \text{ \AA}$. The geometry and ligand orientation are controlled by inter-ligand interactions for both compounds. The structure of $\text{Ga}(\text{tBu})_3$ as determined by *ab initio* calculations [MP2/6-31G(*) level] is in good agreement with the electron diffraction structure. A comparison of the *ab initio* calculated structure [MP2/6-31G(*)] of $\text{In}(\text{tBu})_3$ with the structures of $\text{Al}(\text{tBu})_3$ and $\text{Ga}(\text{tBu})_3$ suggests the formers photochemistry is not due to structural factors.

Reaction of $\text{Ga}(\text{tBu})_3$ with the 1,3-diphenylamidine $[\text{PhN}(\text{H})\text{C}(\text{H})=\text{NPh}]$, H-dpam] yields monomeric $(\text{tBu})_2\text{Ga}(\text{dpam})$ (**38**). The partial hydrolysis of **38** results in the isolation of $(\text{tBu})_2\text{Ga}(\mu\text{-dpam})(\mu\text{-OH})\text{Ga}(\text{tBu})_2$ (**39**), whose structure consists of a gallium dimer in which the amidine and hydroxide ligands bridge two $\text{Ga}(\text{tBu})_2$ moieties. Reaction of $[\text{Me}_2\text{Ga}(\mu\text{-Cl})]_2$ with H-dpam results in the complex $[\text{H}_2\text{-dpam}][\text{Me}_2\text{GaCl}_2]$ (**40**). The solid state structure of **40** indicates the presence of a hydrogen bonded cation-anion complex, in which the core has a twisted eight-membered ring configuration. The versatility of amidines as both chelating and bridging ligands to gallium is discussed with respect to the predominance of bridging and chelating modes of coordination of carboxylates and triazenides, respectively. Reaction of 2-(methylamino)pyridine (H-map) with $\text{Ga}(\text{tBu})_3$ allows for the isolation of $(\text{tBu})_2\text{Ga}(\text{map})$ (**41**). In contrast, reaction with $[(\text{tBu})_2\text{Ga}(\mu\text{-Cl})]_2$ and $[\text{Me}_2\text{Ga}(\mu\text{-Cl})]_2$ yields the Lewis acid base adducts, $(\text{tBu})_2\text{GaCl}(\text{H-map})$ (**42**) and $\text{Me}_2\text{GaCl}(\text{H-map})$ (**43**), respectively. Reaction of compound **43** with $^n\text{PrNH}_2$ does not result in the deprotonation of the H-map ligand, but ligand metathesis and the formation of $(\text{tBu})_2\text{GaCl}(\text{NH}_2^i\text{Pr})$ (**44**).

Hexanethiol ($\text{C}_6\text{H}_{13}\text{SH}$), phenylphosphonic acid $[\text{PhP}(\text{O})(\text{OH})_2]$, and 3-bromo-benzoic acid ($3\text{-BrC}_6\text{H}_4\text{CO}_2\text{H}$) have been reacted with {100}-GaAs surface which have been pretreated with an acid etch and an ammonium sulfide reactive passivation layer. The chemically reacted surfaces have been characterized by X-ray photoelectron spectroscopy (XPS) and advancing contact angle measurements using H_2O and hexadecane. As predicted from simple model compounds, $[(\text{tBu})_2\text{Ga}(\mu\text{-X})]_2$, the thiol and phosphonic acid ligands allow for uniform surface layers, while the carboxylic acid is geometrically unsuited to binding the surface of GaAs.

Impact/Navy Relevance

We have successfully demonstrated that a molecular model approach to the choice of suitable surface binding groups. This will allow for the passivation and chemical modification of semiconductor nano-particles with the view to the development of new device structures. The control of solid state materials structure and morphology will allow for greater control over properties via chemical synthesis rather than process conditions.

Technology Transfer

No new technology transfer is ongoing.

References

N/A

Subcontractors

None

Productivity

Molecular structure of an unusual gallium phosphate compound containing three-coordinate gallium. A. Keys, S. G. Bott, and A. R. Barron, *J. Chem. Soc., Chem. Commun.*, 1996, 2339.

Molecular structures of $[(\text{tBu})_2\text{Ga}(\mu\text{-O}_2\text{CPh})]_2$, $[(\text{tBu})_2\text{Ga}(\mu\text{-O}_2\text{CC}_6\text{H}_4\text{-3-CN})]_2$, $[(\text{tBu})_2\text{Ga}(\mu\text{-SC}_6\text{H}_5)]_2$: the efficacy of oxygen and sulfur donor ligands for binding to GaAs and GaS surfaces. A. Keys, S. G. Bott, and A. R. Barron, *Polyhedron*, 1998, **17**, 3121.

Liquid precursors for the MOCVD growth of gallium sulfide: $(\text{tBu})_2\text{Ga}(\text{S}_2\text{CNR}_2)$. A. Keys, S. G. Bott, and A. R. Barron, *Chem. Mater.*, 1999, **11**, 3578.

Molecular structures of $(^t\text{Bu})\text{Ga}(\text{S}_2\text{CN}^n\text{Pr}_2)_2$ and $(^i\text{PrO})\text{Ga}(\text{S}_2\text{CNEt}_2)_2$: an example of an unusual ligand pseudorotation. A. Keys, S. G. Bott, and A. R. Barron, *J. Chem. Cryst.*, 1998, **28**, 629.

Tert-butyl compounds of gallium. A. Keys, T. Barbarich, S. G. Bott, and A. R. Barron, *J. Chem. Soc., Dalton Trans.*, 2000, 577.

Vapor phase molecular structure of $\text{Al}(^t\text{Bu})_3$ and $\text{Ga}(^t\text{Bu})_3$. A. Keys, P. T. Brain, R. L. Callender, B. A. Smart, C. A. Morrison, H. E. Robinson, D. W. H. Rankin and A. R. Barron, submitted for publication.

A new class of gallium arsenide transistor: realization through a molecular designed insulator. A. R. Barron, *Materials, Synthesis and Characterization*, Ed. D.L. Peny, Plenum, 1997, **6**, 137.

Solid state structure of $[(^t\text{Bu})_2\text{In}(\mu\text{-Cl})]_\infty$: an unusual saw-tooth polymeric structure. S. L. Stoll, S. G. Bott, and A. R. Barron, *Polyhedron*, 1997, **16**, 1763.

Selenide and selenolate compounds of indium: a comparative study of In-Se bond forming reactions. S. L. Stoll, S. G. Bott, and A. R. Barron, *J. Chem. Soc., Dalton Trans.*, 1997, 1315.

Volatility studies on gallium chalcogenide cubanes: thermal analysis and determination of sublimation enthalpies. E. G. Gillan, S. G. Bott, and A. R. Barron, *Chem. Mater.*, 1997, **9**, 796.

Chemical vapor deposition of hexagonal gallium selenide and telluride thin films from cubane precursors. E. G. Gillan and A. R. Barron, *Chem. Mater.*, 1997, **9**, 3037.

1,3-Diphenylamidine and methylaminopyridine compounds of gallium. Y. Koide, J. A. Francis, S. G. Bott, and A. R. Barron, *Polyhedron*, 1998, **17**, 983.

Metal-organic chemical vapour deposition of indium selenide (InSe) thin films. S. L. Stoll and A. R. Barron, *Chem. Mater.*, 1998, **10**, 650.

Reaction of $[(^t\text{Bu})\text{Ga}(\mu_3\text{-Te})_4]$ with elemental sulfur and selenium: a facile chalcogenide exchange reaction. B. D. Fahlman and A. R. Barron, *Organometallics*, 1998, **17**, 5310.

Molecular structure of $[\text{CpFe}(\text{CO})_2]_3\text{In}$. A. Borovik, S. G. Bott, and A. R. Barron, *J. Chem. Cryst.*, 1998, **28**, 837.

Synthesis and structural characterization of cyclopentadienyliron- and cyclopentadienylmolybdenum-gallium compounds, A. Borovik, S. G. Bott, and A. R. Barron, *Organometallics*, 1999, **18**, 2668.